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(54) Self-formable optical waveguide material composition

(57) Into a mixture solution 2 of a high-refractive-index photo-curable resin A and a low-refractive-index photo-curable resin B, light capable of curing only the resin A is led through an optical fiber 1 so that a cured resin 211 of the resin A having a diameter substantially equal to the diameter of a core portion of the optical fiber is formed so as to extend from a tip of the optical fiber. Then, the residual mixture solution 2 is cured. In this manner, a module having the previously cured high-refractive-index resin 211 as an optical waveguide can be formed easily. On this occasion, the mixed state of the mixture solution 2 can be kept good enough to facilitate the formation of the high-refractive-index resin 211 when the solubility parameter δ_A of the high-refractive-index photo-curable resin A and the solubility parameter δ_B and volume fraction ϕ_B of the low-refractive-index photo-curable resin B satisfy the following expression (4).

$$|\delta_A - \delta_B| < -7.5\phi_B + 6.0 \quad (4)$$

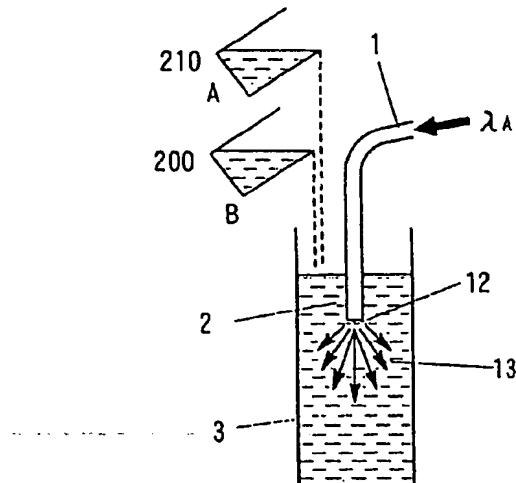
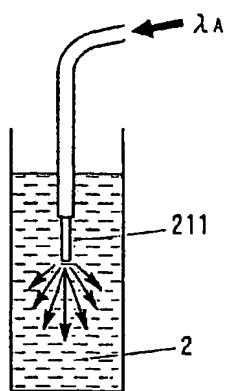
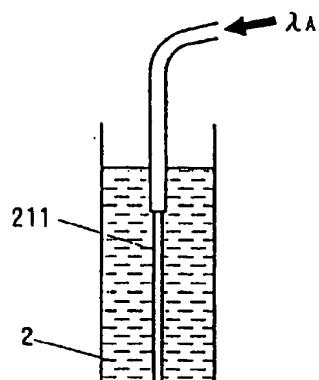


FIG. 1A



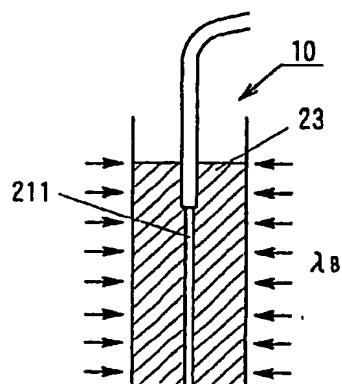
(b)

FIG. 1B



(c)

FIG. 1C



(d)

FIG. 1D

Description

[0001] The present application is based on Japanese Patent Application No. 2001-377957, the entire contents of which are incorporated herein by reference.

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BACKGROUND OF THE INVENTION

[0002] The present invention relates to a self-formable optical waveguide material composition containing two photo-curable resins which have different refractive indices and which can be cured by different wavelengths respectively.

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The concept "photo-curable resin" used in the invention means a monomer, a macro-monomer or an oligomer containing a photo-reaction initiator.

SUMMARY OF THE INVENTION

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[0003] Some of the present inventors have already developed a technique disclosed in Japanese Unexamined Patent Publication No. JP 2000-347043A. The technique is as follows. Into a mixture solution containing a high-refractive-index photo-curable resin and a low-refractive-index photo-curable resin, light to cure only the high-refractive-index photo-curable resin is led through an optical fiber so that a high-refractive-index cured resin having a diameter substantially equal to the diameter of a core portion of the optical fiber is formed in the mixture solution so as extend from a tip of the optical fiber. Then, the residual mixture solution is cured, so that a module having the previously formed high-refractive-index resin as an optical waveguide can be formed easily.

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[0004] This technique will be described with reference to Figs. 1A through 1D. In the condition that a mixture solution 2 containing a high-refractive-index photo-curable resin A 210 and a low-refractive-index photo-curable resin B 200 is put in a vessel 3, a tip of an optical fiber 1 is immersed in the mixture solution (Fig. 1A). Assume now that the high-refractive-index photo-curable resin A can be cured by a wavelength λ_A but the low-refractive-index photo-curable resin B cannot be cured by the wavelength λ_A whereas both the high-refractive-index photo-curable resin A and the low-refractive-index photo-curable resin B can be cured by a wavelength λ_B . This assumption can be satisfied in the relation $\lambda_A > \lambda_B$ and in the case where the high-refractive-index photo-curable resin A and the low-refractive-index photo-curable resin B have different curing mechanisms, i.e., using radical polymerization and ion polymerization respectively.

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[0005] When optical waveguide-forming light at the wavelength λ_A is led into the optical fiber 1 in the aforementioned condition, only the high-refractive-index photo-curable resin A in the mixture solution 2 is cured at the tip of the optical fiber 1 to thereby grow a cylindrical cured resin 211 successively (Fig. 1B). This is because the curing of the low-refractive-index photo-curable resin B is not initiated by light at the wavelength λ_A so that the low-refractive-index photo-curable resin B is not copolymerized with the high-refractive-index photo-curable resin A. After the growth of the cylindrical cured resin 211 with a required length is completed thus (Fig. 1C), both the high-refractive-index photo-curable resin A and the low-refractive-index photo-curable resin B in a mixed state are cured by light at the wavelength λ_B given from the outside. As a result, there is obtained a cured resin 23 which is not a copolymer but has a refractive index between refractive indices of two cured resins which can be obtained when the high-refractive-index photo-curable resin A and the low-refractive-index photo-curable resin B are cured singly respectively. In this manner, the cylindrical cured resin 211 having a high refractive index and the cured resin 23 having a refractive index lower than that of the cylindrical cured resin 211 can form an optical waveguide (Fig. 1D).

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[0006] While the inventors was further developing this technique, the inventors found that the mixed state of the high-refractive-index photo-curable resin A and the low-refractive-index photo-curable resin B before curing is very important. That is, in the optical waveguide constituted by the cylindrical cured resin 211 having a high refractive index and the cured resin 23 having a refractive index lower than that of the cylindrical cured resin 211, leakage loss can be reduced as the refractive index difference between the two cured resins 211 and 23 increases. This means the fact that the high-refractive-index photo-curable resin A and the low-refractive-index photo-curable resin B before curing are largely different from each other in terms of chemical structure. Hence, the mixed state is apt to become poor to cause a phenomenon that the mixture solution 2 turns white turbidly. When the mixture solution 2 turns white turbidly, optical waveguide-forming light in a photo-polymerization reactive portion is scattered to make the formation of the cylindrical cured resin 211 so insufficient that the cylindrical cured resin 211 can little grow occasionally. In addition, if the amount of the high-refractive-index photo-curable resin A is extremely smaller than the amount of the low-refractive-index photo-curable resin B, the cylindrical cured resin 211 still little grows.

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[0007] In order to solve the problem, an object of the invention is to find an appropriate combination of a high-refractive-index photo-curable resin A and a low-refractive-index photo-curable resin B by estimating solubility parameters of the two photo-curable resins A and B before curing. Another object of the invention is to find an appropriate composition on the basis of the relation in solubility parameter and volume fraction between a high-refractive-index

photo-curable resin A and a low-refractive-index photo-curable resin B before curing.

[0008] According to an aspect of the invention, there is provided a self-formable optical waveguide material composition containing a first photo-curable resin which can be cured by a certain wavelength, and a second photo-curable resin which is not cured by the certain wavelength but can be cured by another wavelength, wherein the self-formable optical waveguide material composition satisfies the expression (1):

$$|\delta_A - \delta_B| < 6.0 \quad (1)$$

10 in which δ_A is a solubility parameter of the first photo-curable resin expressed in MPa^{1/2}, and δ_B is a solubility parameter of the second photo-curable resin expressed in MPa^{1/2}.

[0009] Incidentally, the relation 2 MPa^{1/2} ≈ 1 cal^{1/2}/cm^{3/2} holds hereinafter.

[0010] According to another aspect of the invention, the self-formable optical waveguide material composition satisfies the expression (2) or (3):

$$|\delta_A - \delta_B| < 5.0 \quad (2)$$

$$|\delta_A - \delta_B| < 4.0 \quad (3)$$

[0011] According to a further aspect of the invention, the ratio of the refractive index of the first photo-curable resin before curing to the refractive index of the second photo-curable resin before curing is higher than 1 but not higher than 1.14, and the volume fraction of the second photo-curable resin is not lower than 0.01 but lower than 0.8. Incidentally, this hereinafter means the fact that the refractive index of the first photo-curable resin before curing is not higher than 1.14 times as high as the refractive index of the second photo-curable resin before curing. On the other hand, the volume fraction of the second photo-curable resin means the ratio of the volume of the second photo-curable resin to the sum of the volume of the first photo-curable resin and the volume of the second photo-curable resin before mixing. Especially preferably, the volume fraction is selected to be not lower than 0.1.

[0012] According to a further aspect of the invention, there is provided a self-formable optical waveguide material composition containing a first photo-curable resin which can be cured by a certain wavelength, and a second photo-curable resin which is not cured by the certain wavelength but can be cured by another wavelength, wherein: the ratio of the refractive index of the first photo-curable resin before curing to the refractive index of the second photo-curable resin before curing is higher than 1 but not higher than 1.14; and the self-formable optical waveguide material composition satisfies the expression (4):

$$|\delta_A - \delta_B| < -7.5\Phi_B + 6.0 \quad (4)$$

40 in which δ_A is a solubility parameter of the first photo-curable resin expressed in MPa^{1/2}, δ_B is a solubility parameter of the second photo-curable resin expressed in MPa^{1/2}, and Φ_B ($\Phi_B \geq 0.01$) is a volume fraction of the second photo-curable resin. Especially preferably, the volume fraction Φ_B is selected to be not lower than 0.1.

[0013] According to a further aspect of the invention, the self-formable optical waveguide material composition satisfies the expression (5) or (6):

$$|\delta_A - \delta_B| < -7.5\Phi_B + 5.0 \quad (5)$$

$$|\delta_A - \delta_B| < -7.5\Phi_B + 4.0 \quad (6)$$

[0014] The inventors have found that the relation between the solubility parameter of the first photo-curable resin and the solubility parameter of the second photo-curable resin plays an important role in this subject of matter as will be described in the following embodiments. That is, it has been found that there is a large difference in optical waveguide-forming speed between the case where the restrictive item of each aspect of the invention is satisfied and the case where the restrictive item is not satisfied. This means the fact that it is important to provide a combination of the first photo-curable resin and the second photo-curable resin easily soluble in each other. That is, the condition that

the two photo-curable resins are mixed well is essential for curing only the first photo-curable resin. The relation between the mixed state and the volume fraction, that is, the mixture ratio is more remarkable.

BRIEF DESCRIPTION OF THE DRAWINGS

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[0015]

Figs. 1A to 1D are process views showing an optical waveguide-forming method to which the invention is applied; Fig. 2 is a graph showing the relation between the absolute value of solubility parameter difference and the relative length of the cured resin obtained by curing a high-refractive-index photo-curable resin; Fig. 3 is a graph showing the relation between the volume fraction of a low-refractive-index photo-curable resin and the relative length of the cured resin obtained by curing a high-refractive-index photo-curable resin M1100; Fig. 4 is a graph showing the relation between the volume fraction of a low-refractive-index photo-curable resin and the relative length of the cured resin obtained by curing a high-refractive-index photo-curable resin M210; Fig. 5 is a graph showing the relation between the volume fraction of a low-refractive-index photo-curable resin and the relative length of the cured resin obtained by curing a high-refractive-index photo-curable resin M6200; and Fig. 6 is a graph showing the relation between the volume fraction Φ_B of a low-refractive-index photo-curable resin B and the absolute value of solubility parameter difference in the case where the relative length of the cured resin is taken as a point in the graph.

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DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0016] Data indicating the effectiveness of the invention will be described below. Resins, etc. used for obtaining the data are as follows. Hereinafter, names of articles in Table 1 are abbreviated as M1100, M210, M6200, OXT101, OXT221, OXT212 and 2021P in order. Incidentally, each of M1100, M210 and M6200 contains no polymerization initiator. Therefore, each of M1100, M210 and M6200 mixed with 1 % of Irgacure 819 (bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide) made by Ciba Speciality Chemicals Inc. is used as a high-refractive-index photo-curable resin A. Incidentally, solubility parameters are calculated by the Small et al. calculation method described in Polymer Handbook 4th edition pp.682-685 published by Wiley Interscience and on the basis of data therefor (the same book, the same pages, table 1-3).

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Table 1

In Table 1, n_D means a refractive index on the basis of D-line of Na.

High-Refractive-Index Photo-Curable Resin A (each made by Toagosei Co., Ltd.)			
Product Name	n_D	δ_A	Content
ARONIX M-1100	1.490	22.10	Urethane denatured acrylate
ARONIX M-210	1.536	20.84	Bisphenol A/ EO denatured diacrylate
ARONIX M-6200	1.519	22.70	Polyester acrylate

Low-Refractive-Index Photo-Curable Resin B (each made by Toagosei Co., Ltd.)			
Product Name	n_D	δ_A	Content
OXT-101	1.453	23.72	3-ethyl-3-hydroxymethyloxetane
OXT-221	1.456	18.25	Di[1-ethyl(3-oxetanyl)]methyl ether
OXT-212	1.442	17.10	3-ethyl-3-(2-ethylhexyloxymethyl)oxetane

Low-Refractive-Index Photo-Curable Resin B (made by Daicel Chemical Industries, Ltd.)			
Product Name	n_D	δ_A	Content
Celoxide 2021P	1.497	23.44	Alicyclic epoxy compound

Solvent	n_D	δ_A
Metanol	1.327	28.17
Hexane	1.372	14.90
Heptane	1.385	15.21

[0017] In Table 1, curing of the high-refractive-index photo-curable resin A in the presence of the polymerization initiator therefor is radical polymerization. For this reason, the low-refractive-index photo-curable resin B mainly subjected to ring-opening polymerization by cationic polymerization is not copolymerized with the high-refractive-index photo-curable resin A. Thus, in 18 combinations of the high-refractive-index photo-curable resin A and the low-refractive-index photo-curable resin B or a solvent in Table 1, the curing speed of the high-refractive-index photo-curable resin A to form a core of an optical waveguide was observed in the condition that the volume fraction of the high-refractive-index photo-curable resin A was 0.8. That is, in a reaction system shown in Figs. 1A to 1D, the length of the cured resin 211 obtained by irradiation with light for a predetermined time was measured. The solvent was not equivalent to the low-refractive-index photo-curable resin B but was used as a material substituted for the low-refractive-index

photo-curable resin B for the sake of convenience in order to verify materials having various solubility parameters. An optical fiber 1 having a core diameter of 730 μm , a clad diameter of 750 μm and a numerical aperture of 0.25 was used. Monochromatic light at a wavelength of 488 nm was used as incident light. Results of the measurement were as shown in Fig. 2. In Fig. 2, the vertical axis was taken to express the relative length of the cured resin 211 whereas the horizontal axis was taken to express the absolute value of solubility parameter difference. The relative length was calculated as follows. In the condition that each of M1100, M210 and M6200 as the high-refractive-index photo-curable resin A was put singly in a vessel 3 shown in Figs. 1A to 1D, the time required for the length of the cured resin 211 to reach 20 mm was measured as irradiation time in each mixture. In each composition to be tested, the length (mm) of the cured resin 211 formed for the irradiation time was measured and divided by 20. The resulting value was obtained as the relative length. When any one of M1100, M210 and M6200 was used as the high-refractive-index photo-curable resin A, the cured resin serving as a core of an optical waveguide was not formed at all if the absolute value of solubility parameter difference was larger than 6.0. When any one of M1100, M210 and M6200 was used as the high-refractive-index photo-curable resin A, the relative length of the cured resin serving as a core of an optical waveguide became noticeably large if the absolute value of the solubility parameter difference between the high-refractive-index photo-curable resin A and the low-refractive-index photo-curable resin B or solvent mixed therewith was not larger than 5.0. The relative length of the cured resin serving as a core of an optical waveguide became further larger if the absolute value of solubility parameter difference was not larger than 4.0.

[0018] In each of Figs. 3, 4 and 5, the vertical axis was taken to express the relative length of the cured resin 211 whereas the horizontal axis was taken to express the compounding ratio (volume fraction) of the low-refractive-index photo-curable resin B. The relative length was calculated as follows. Four low-refractive-index photo-curable resins B were one by one combined with a high-refractive-index photo-curable resin A to thereby form four combinations. While the compounding ratio (volume fraction) of each of the four combinations was changed, the length (mm) of the cured resin 211 was measured and divided by 20. The resulting value was obtained as the relative length of the cured resin 211. In any case, only a very short cured resin 211 was formed when the volume fraction Φ_B of the low-refractive-index photo-curable resin B was not lower than 0.8.

[0019] Fig. 6 shows data obtained in Figs. 3, 4 and 5. In Fig. 6, the horizontal axis was taken to express the volume fraction Φ_B of the low-refractive-index photo-curable resin B whereas the vertical axis was taken to express the absolute value of solubility parameter difference. In Fig. 6, each point expresses the relative length of the cured resin 211. From the points, there was deduced the relation between the volume fraction Φ_B of the low-refractive-index photo-curable resin B and the absolute value of solubility parameter difference to make the relative length of the cured resin 211 not smaller than a predetermined value. The relation was as follows. A composition satisfying the expression (5) is preferable to a composition satisfying the expression (4). A composition satisfying the expression (6) is preferable to the composition satisfying the expression (5).

$$|\delta_A - \delta_B| < -7.5\Phi_B + 6.0 \quad (4)$$

$$|\delta_A - \delta_B| < -7.5\Phi_B + 5.0 \quad (5)$$

$$|\delta_A - \delta_B| < -7.5\Phi_B + 4.0 \quad (6)$$

[0020] The photo-polymerization initiator and the monomer or oligomer which can be preferably used in the method for producing an optical waveguide according to the invention are, for example, as follows.

[0021] As a monomer subjected to radical photo-polymerization, (meth) acrylic ester or (meth) acrylamide may be preferably used. Specifically, there can be used monofunctional (meth)acrylic ester (mono(meth)acrylate) such as 2-ethylhexyl (meth)acrylate, cyclohexyl (meth)acrylate or 2-butoxyethyl (meth)acrylate. There can be also used ester of diol and bivalent (meth)acrylate (di(meth)acrylate) such as ethylene glycol, neopentyl glycol or 1,6-hexanediol. There can be further used ester of (meth)acrylic acid and an organic compound having a plurality of alcoholic hydroxyl groups (tri, tetra, ... (meth)acrylate). Incidentally, methyl-hydrogen, methylene-hydrogen and methine-hydrogen in (meth)acryloyl groups and other organic skeletons in these monomers may be partially replaced by halogen. Further, these monomers may be used in combination suitably.

[0022] As an oligomer (macromonomer) subjected to radical photo-polymerization, there can be preferably used an urethane oligomer, a polyether oligomer, an epoxy oligomer, a polyester oligomer or the like, having a (meth)acryloyl group at a terminal or branch. Incidentally, methyl-hydrogen, methylene-hydrogen and methine-hydrogen in (meth)acryloyl groups and other organic skeletons in these oligomers may be partially replaced by halogen. Further, these

oligomers combined with the aforementioned monomers suitably may be used.

[0023] As a radical photo-polymerization initiator, there can be used: a benzylidemethylketal compound such as 2,2-dimethoxy-2-phenylacetophenone; an α -hydroxyketone compound such as 2-hydroxy-2-methyl-phenylpropane-1-one or (1-hydroxycyclohexyl)-phenylketone; an α -aminoketone compound such as 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butane-1-one or 2-methyl-1-(4-(methylthio)phenyl)-2-morpholinopropane-1-one; a bisacylphosphine oxide compound such as bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylbentylphosphine oxide or bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide; a metallocene compound such as bis (η -cyclopentadienyl)-bis(2,6-difluoro-3-(N-pyrrol)phenyl)titanium; and so on. Several kinds selected from these aforementioned radical photo-polymerization initiators may be used.

[0024] As a monomer or oligomer subjected to cationic photo-polymerization, there can be used: a compound having cyclic ether such as an epoxy ring or an oxetane ring; a cyclic lactone compound; a cyclic acetal compound; a vinyl ether compound; and so on. These monomers or oligomers may be used in combination suitably.

[0025] As a cationic photo-polymerization initiator, there can be used: 4,4'-bis(di(2-hydroxyethoxy)phenylsulfonio)phenylsulfide bihexafluoroantimonate; η -cyclopentadienyl- η -cumene iron(I+)-hexafluorophosphate(1-); and so on.

[0026] A photosensitizer may be added into the radical photo-polymerization initiator or the cationic photo-polymerization initiator. Additives such as a polymerization inhibitor, an ultraviolet absorber, a light stabilizer, an oxidation inhibitor, a leveling agent, and an anti-foaming agent may be further mixed as occasion demands. A photo-curable liquid resin composition used in the invention can be constituted by the aforementioned combination. Further, a combination of an anionic photo-polymerization initiator and a monomer or oligomer is not excluded from the invention.

Polymerization due to thiol-ene addition may be also used. On the assumption that a core portion is formed by irradiation with light in the same manner as in the invention, a clad portion may be formed by another method than irradiation with light.

[0027] It is explicitly stated that all features disclosed in the description and/or the claims are intended to be disclosed separately and independently from each other for the purpose of original disclosure as well as for the purpose of restricting the claimed invention independent of the compositions of the features in the embodiments and/or the claims. It is explicitly stated that all value ranges or indications of groups of entities disclose every possible intermediate value or intermediate entity for the purpose of original disclosure as well as for the purpose of restricting the claimed invention.

Claims

1. A self-formable optical waveguide material composition containing a first photo-curable resin which can be cured by a certain wavelength, and a second photo-curable resin which is not cured by the certain wavelength but can be cured by another wavelength, characterized in that said self-formable optical waveguide material composition satisfies the expression (1):

$$|\delta_A - \delta_B| < 6.0 \quad (1)$$

wherein δ_A is a solubility parameter of said first photo-curable resin expressed in MPa^{1/2}, and δ_B is a solubility parameter of said second photo-curable resin expressed in MPa^{1/2}.

2. A self-formable optical waveguide material composition according to Claim 1, wherein said self-formable optical waveguide material composition satisfies the expression (2) :

$$|\delta_A - \delta_B| < 5.0 \quad (2)$$

3. A self-formable optical waveguide material composition according to Claim 1, wherein said self-formable optical waveguide material composition satisfies the expression (3) :

$$|\delta_A - \delta_B| < 4.0 \quad (3)$$

4. A self-formable optical waveguide material composition according to any one of Claims 1 through 3, wherein:

a ratio of a refractive index of said first photo-curable resin before curing to a refractive index of said second

photo-curable resin before curing is higher than 1 but not higher than 1.14; and
 a volume fraction of said second photo-curable resin is not lower than 0.01 but lower than 0.8.

- 5 5. A self-formable optical waveguide material composition containing a first photo-curable resin which can be cured by a certain wavelength, and a second photo-curable resin which is not cured by the certain wavelength but can be cured by another wavelength, **characterized in that:**

a ratio of a refractive index of said first photo-curable resin before curing to a refractive index of said second photo-curable resin before curing is higher than 1 but not higher than 1.14; and
 10 said self-formable optical waveguide material composition satisfies the expression (4) :

$$|\delta_A - \delta_B| < -7.5\Phi_B + 6.0 \quad (4)$$

15 in which δ_A is a solubility parameter of said first photo-curable resin expressed in MPa^{1/2}, δ_B is a solubility parameter of said second photo-curable resin expressed in MPa^{1/2}, and Φ_B ($\Phi_B \geq 0.01$) is a volume fraction of said second photo-curable resin.

- 20 6. A self-formable optical waveguide material composition according to Claim 5, wherein said self-formable optical waveguide material composition satisfies the expression (5) :

$$|\delta_A - \delta_B| < -7.5\Phi_B + 5.0 \quad (5)$$

- 25 7. A self-formable optical waveguide material composition according to Claim 5, wherein said self-formable optical waveguide material composition satisfies the expression (6) :

$$|\delta_A - \delta_B| < -7.5\Phi_B + 4.0 \quad (6)$$

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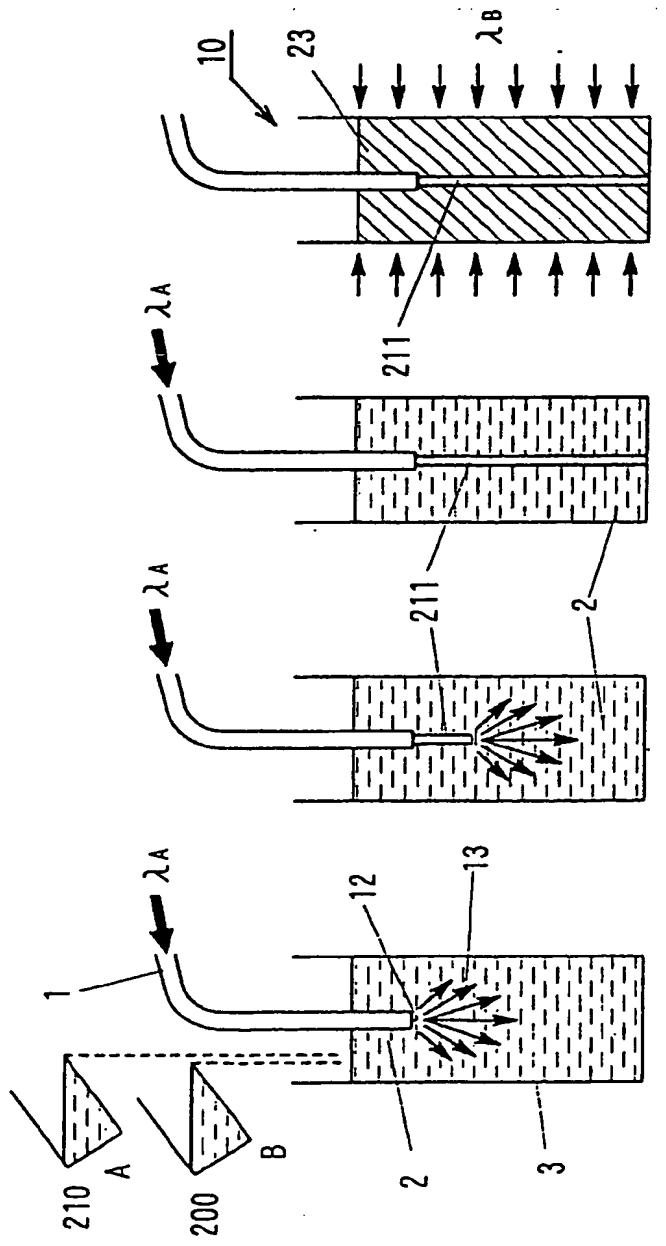
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(a) FIG. 1A
 (b) FIG. 1B
 (c) FIG. 1C
 (d) FIG. 1D

FIG. 2

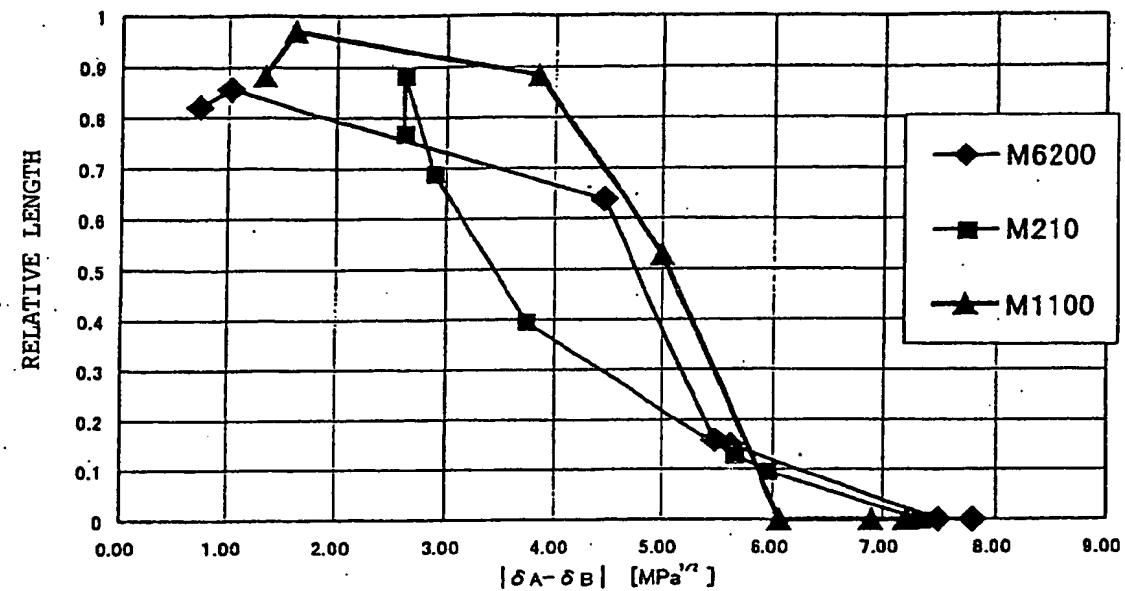


FIG. 3

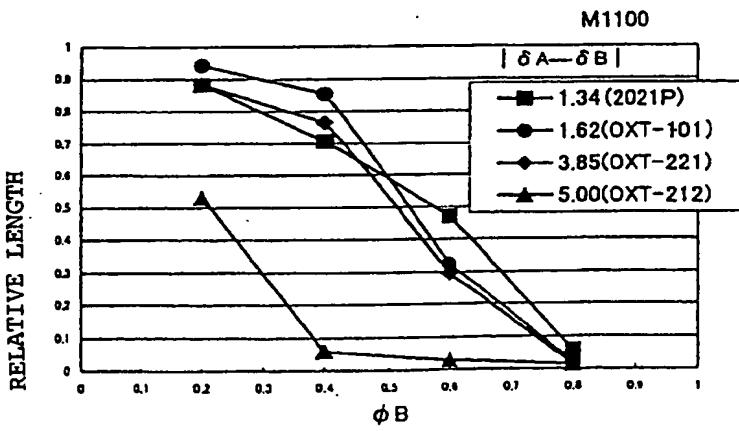


FIG. 4

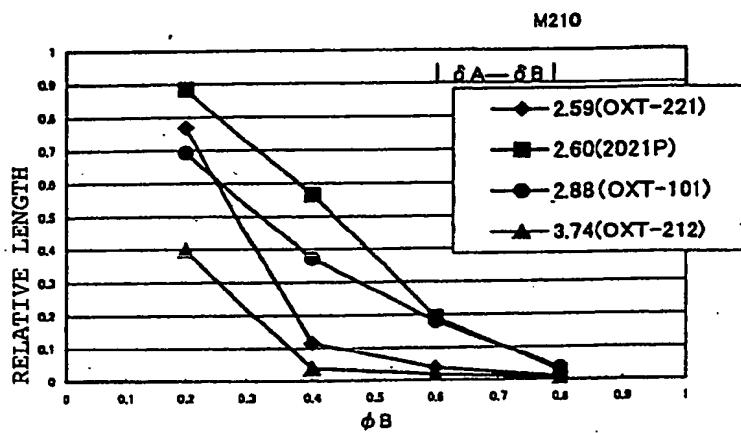


FIG. 5

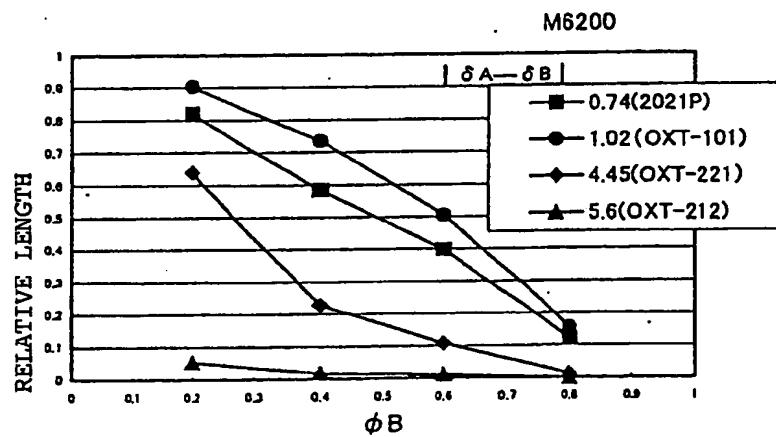
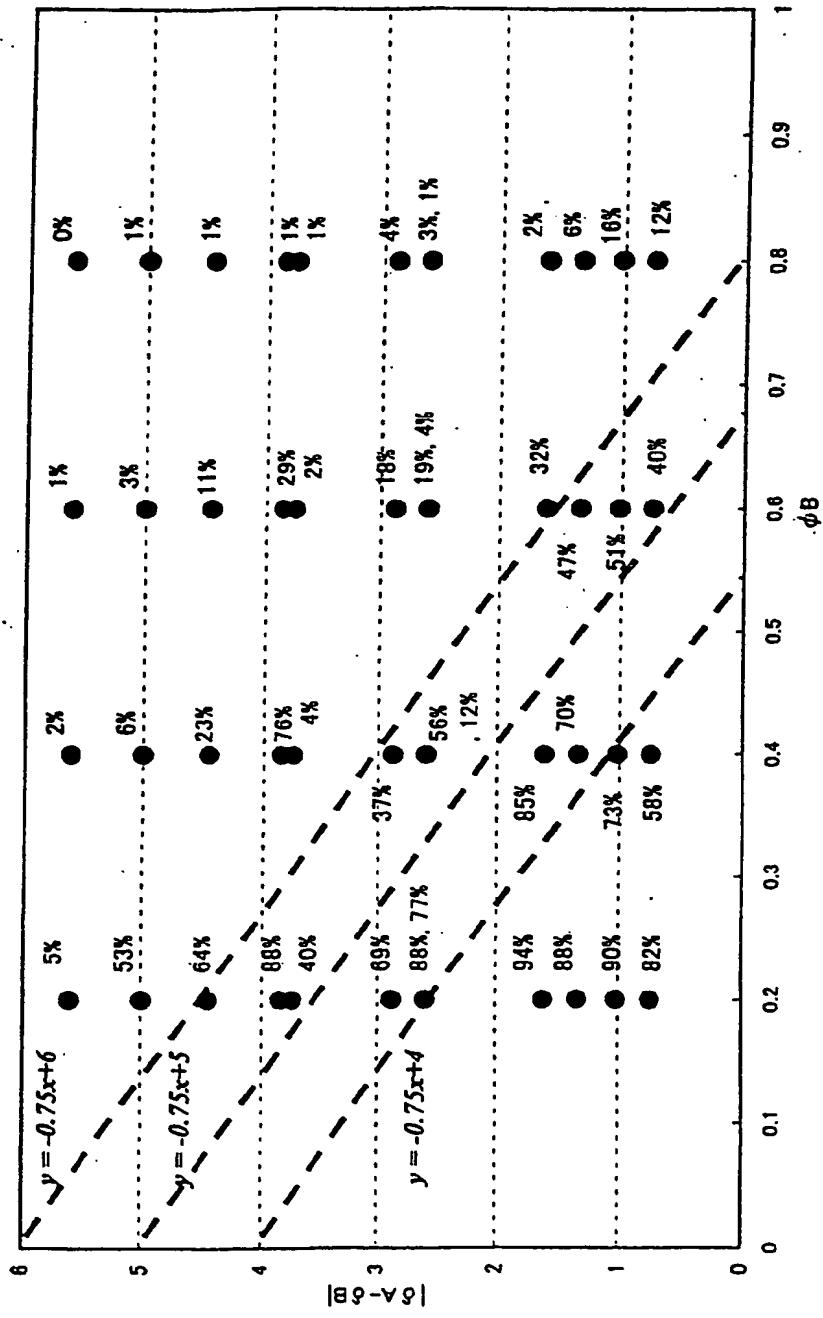


FIG. 6





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(54) Self-formable optical waveguide material composition

(57) Into a mixture solution 2 of a high-refractive-index photo-curable resin A and a low-refractive-index photo-curable resin B, light capable of curing only the resin A is led through an optical fiber 1 so that a cured resin 211 of the resin A having a diameter substantially equal to the diameter of a core portion of the optical fiber is formed so as to extend from a tip of the optical fiber. Then, the residual mixture solution 2 is cured. In this manner, a module having the previously cured high-refractive-index resin 211 as an optical waveguide can be formed easily. On this occasion, the mixed state of the mixture solution 2 can be kept good enough to facilitate the formation of the high-refractive-index resin 211 when the solubility parameter δ_A of the high-refractive-index photo-curable resin A and the solubility parameter δ_B and volume fraction ϕ_B of the low-refractive-index photo-curable resin B satisfy the following expression (4).

$$|\delta_A - \delta_B| < -7.5\phi_B + 6.0 \quad (4)$$

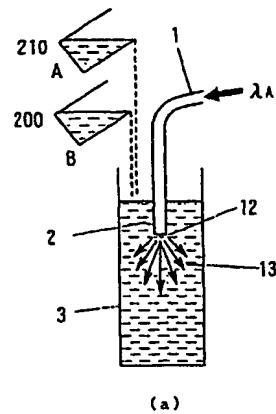
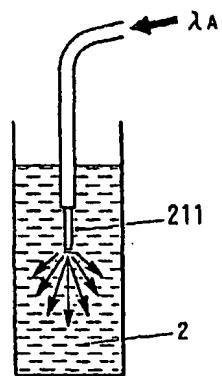
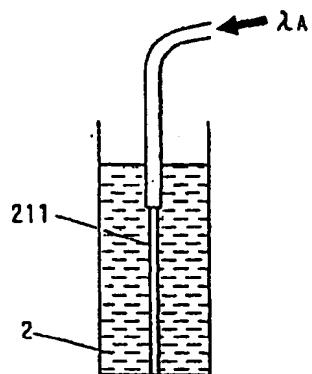


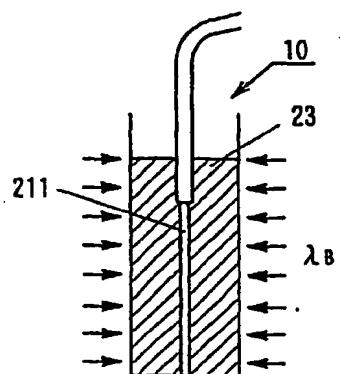
FIG. 1A



(b)
FIG. 1B



(c)
FIG. 1C



(d)
FIG. 1D



European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 02 02 7708

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<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>MUNICH</td> <td>4 July 2003</td> <td>Orignac, X</td> </tr> </table> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>				Place of search	Date of completion of the search	Examiner	MUNICH	4 July 2003	Orignac, X
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**ANNEX TO THE EUROPEAN SEARCH REPORT
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EP 02 02 7708

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